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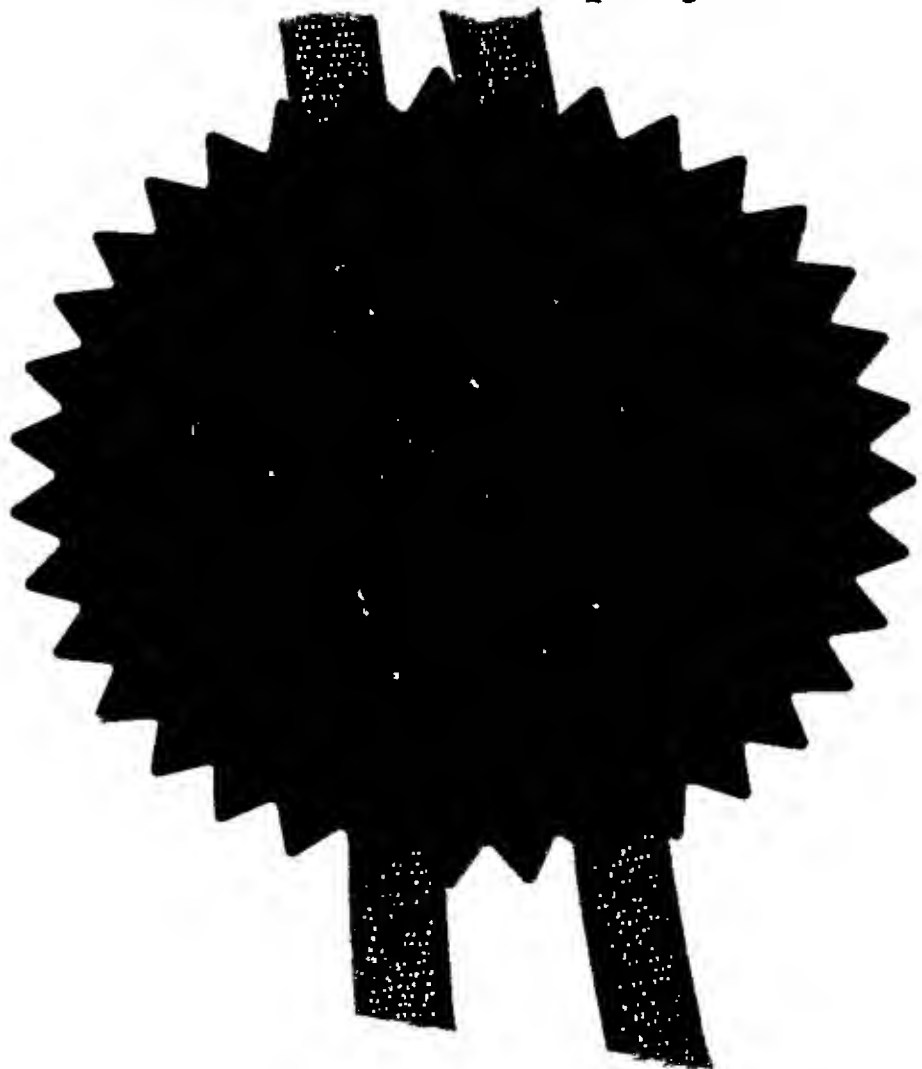
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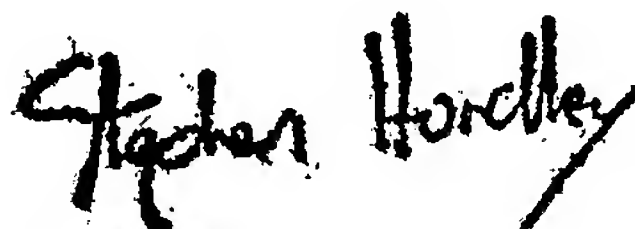
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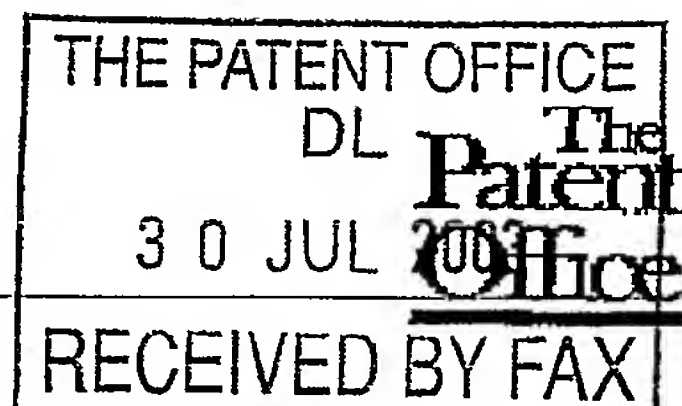


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Patents ADP number (if you know it)

Sherwood Technology Ltd.
Unit 3, Wheldon Road
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WA8 8FW

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

LASER-MARKABLE COMPOSITIONS

5. Name of your agent (if you have one)

Gill Jennings & Every

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Broadgate House
7 Eldon Street
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Claim(s)

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11. For the applicant
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LASER-MARKABLE COMPOSITIONS

Field of the Invention

This invention relates to a composition that can be extruded or formulated as a lacquer and is also capable of being printed by use of a laser.

5 Background of the Invention

Various proposals have been made, in order to achieve effective printing on a substrate, by causing a change of colour in the substrate on which the printing is to appear. Various pigments have been proposed, which can be used to mark a substrate on the application of laser energy. Some of these proposals
10 may be found in, for example, WO-A-00/43456, JP-A-11001065, EP-A-0522370, EP-A-0797511, US-A-5053440, US-A-5350792 (a plastics moulding composition comprising a polyoxymethylene and animal charcoal), US-A-5928780, US-A-6017972 and US-A-6019831. US-A-5489639 and US-A-5884079 disclose that copper hydroxy phosphate is a laser-markable material.

15 Ammonium octamolybdate, having the formula $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26}$ and abbreviated herein as AOM, is a readily available material that has fire-retardant properties. For this purpose, it has been formulated with polymers such as polyvinyl chloride (PVC). For example, PVC-containing cables may contain AOM as a smoke-suppressing agent. AOM is an example of an oxyanion of a
20 multivalent metal; many compounds of this type exist in coloured lower valence or non-stoichiometric states.

Printing on packaging such as cartonboard is of considerable commercial importance. This may be simply to provide visible information to a person handling the packages, but is also required for bar-coding and other marking that
25 is intended to be read by machine. This entails two particular problems.

Firstly, the most economical packaging material tends to be brown or some other indeterminate colour, against which bar-coding in, say, black has low contrast (typically grade C or D). Secondly, because of the need to customise packaging, there is wastage involved in printing information on packaging that
30 has to be adapted for each particular customer.

Summary of the Invention

It has been found that many oxyanions in combination with polymer binders absorb at the wavelength of CO₂ laser light (10,600 nm) and undergo a colour change due to a change in oxidation state, but are not affected by ultraviolet light (commonly used for polymer curing) or by the temperatures, typically around 200-300°C, used in extrusion. AOM behaves in this way. It is thus effectively laser-selective, and provides a very suitable material for use in inks intended for application to surfaces which may be required to undergo a heat treatment or for incorporation into polymer extrusions, and be marked by the application of laser light.

According to one aspect of the present invention, an ink composition comprises:

- a solvent;
- a binder, preferably but not essentially having a labile group; and
- an oxyanion of a multivalent metal.

According to a further aspect of the invention, a polymer laminate or extrudate incorporates a laser-markable material such as an oxyanion of a multivalent metal. This is useful for producing tamper-proof labels.

According to yet another aspect of the present invention, a method for providing an image on a substrate comprises applying, to a relatively small area of the substrate, a formulation comprising a pigment and a component that forms an image on irradiation with laser light, wherein the image has greater contrast with respect to the pigment than with respect to the substrate. As in other aspects of the invention, the component may be an oxyanion of a multivalent metal.

This method allows high contrast to be achieved (typically grade A or B) between the image and its immediate background. Further, the fact that the image can be provided on demand, and is not dependent on the supply of the substrate, means that the wastage inherent in customisation can be avoided; this can lead to substantial savings in cost, for packaging produced in high volume.

Description of Preferred Embodiments

In an oxyanion-containing compound for use in the invention, the cation may be ammonium or an alkali or alkaline earth metal, but is not critical. The oxyanion may be a molybdate, tungstate or analogous transition metal compound.

5 Such compounds include di- and hepta-molybdates. The compound is preferably AOM; the following description refers to AOM for the purposes of illustration only. Currently, AOM is preferred because it is readily available, and is selective for a robust, low-power CO₂ laser operating at about 10,600 nm.

An ink formulation to be used in the invention may be water-based, solvent-based, or UV-curable, and it may be a solution or dispersion. The

10 formulation may include a chargeable component, for use in an ink jet printer.

The binder and the AOM are intimately mixed with the solvent which may be selected from those usually used for inks and lacquers, e.g. water, ethanol, ethyl acetate, isopropyl alcohol, hydrocarbons, etc. The components may be

15 present in solution and/or dispersion. The amount of the AOM in the ink is typically 1 to 90% by weight. The binder is typically polymeric, and may be selected from commercially-available polymers including acrylics, celluloses, PVOH, polyesters, etc. The binder preferably includes a labile group such as hydroxyl, acetoxyl, ether acetal or halogen and this has the function of

20 undergoing elimination reaction, to give a colour-forming entity (see also WO-A-02/068205 and US Patent Application No. 10/344,393, the contents of which are incorporated herein by reference).

AOM can be incorporated into various polymer systems and milled, using a bead mill, to a desired particle size, without any technical difficulty. Examples

25 of polymer systems in which AOM has been successfully incorporated and milled include nitrocellulose solution in alcohol/ethyl acetate, cellulose acetate propionate solution in alcohol/ethyl acetate, polyvinyl butyral solution in alcohol/ethyl acetate, solvent-based polyurethane resin, solvent-based epoxide resin, solvent-based polyester resin, water-based acrylic resin, water-based

30 polyester resin, water-based polyurethane resin, solventless ultra violet light curable monomers and oligomers, solvent-based polyamides, solvent-based

polyimides, water-based polyamides, water-based polyimides, solvent-based epoxy/vinyl/polyester coatings and lacquers, and siloxane resins.

Organic and inorganic pigments can be incorporated into AOM inks/coatings without any adverse effect on the laser markability of the AOM inks/coatings. Further, the AOM inks/coatings containing the organic and inorganic pigments can be milled to desired particle size without difficulty or adverse affect on the laser markability of AOM inks/coatings.

The AOM component may alternatively be melt-incorporated into extrudable polymers, or it may be incorporated into UV-cure monomer formulations. A film or laminate of layers which include a laser-markable component provides a tamper-proof product. Extrudable polymers which can be used in the invention include nylon, polyesters, polyamide, polycarbonate, polyacrylate, polymethacrylate, ABS graft polymers, polyolefins such as polyethylene or polypropylene, polystyrene, polyvinyl chloride, polyoxymethylene, polyimide, polyethers and polyether ketones, thermoplastic elastomers, thermoplastic polyurethane which may be used individually or as a blend of various polymers, are suitable as the polymer matrix. The amount of AOM that is incorporated is typically 0.1 to 5% by weight of the extrudate.

The AOM or analogue thereof may be laser-selective, by which is meant that it absorbs energy at a wavelength, e.g. of ~1064 nm or ~10600 nm, for which a laser can be chosen accordingly, such that it undergoes a colour change. The colour change will typically be the result of a change in valence state and/or the formation of non-stoichiometric products, although there may also be some reaction with the binder. The laser that is used can operate in either the dot matrix mode or continuous-wave, scribing mode.

The substrate may be board, e.g. cartonboard. Packaging that may be used in the invention may alternatively be in the form of a polymeric film, such as polypropylene or polyethylene, and which may be laminated and used, for example, for wrapping chocolate. If a multi-layer packaging material is used, the invention is applicable at whatever layer the ink is present.

Any pigment that is used in the invention may be conventional. A white pigment may be preferred, providing not only contrast with, say, black bar-coding

but also opacity. Other colours may be chosen, as desired. Typical pigments include CaCO_3 , ZnO , TiO_2 and talc.

A formulation of the invention may also include conventional components that are present in order to provide the image. Typically, they include a material
5 that absorbs incident laser light; this material may itself change colour on absorption, or may react with another material to provide a change of colour. Typical reactants include phenols, phenolic resins, carboxylic acids together with a colour-former, e.g. Crystal Violet Lactone. Typical absorbing agents include
clays, micas, TiO_2 , carbonates, oxides, talc, silicates and aluminosilicates.

10 It will be appreciated by one of ordinary skill in the art that it is possible to incorporate additives of various sorts in the imaging layers, and which might be beneficial in certain circumstances. Such additives include, for example, polymer binders, mild reducing agents to promote thermal printer performance, colorants such as dyes or pigments, antioxidants and other known stabilisers,
15 antiblocking materials such as talc or selected silicas, and materials adsorbent to or reactive with any thermolysis products of laser imaging.

An additive of particular utility, in solution or suspension or in a separate layer, is an electron-donating dye precursor often known as a colour-former. When amine molybdates are incorporated in a layer with such colour-formers
20 and thermally imaged, e.g. using a CO_2 laser, coloured images may be obtained. The colour may correspond to that obtained by the use of common colour developers such as certain phenols. Weak block images may also be obtained, e.g. using a heat sealer at 100-120 C and contact times of 1-10 seconds. Thus the amine molybdate acts as an electron acceptor and colour developer for at
25 least some of these colour-formers. The low melting point of amine molybdates means that they can be fused with colour-formers, if desired.

Protective polymer or other layers on the imaging layer may be useful in some circumstances. For example, such layers may prevent or reduce mechanical or chemical damage to the unexposed or exposed thermally
30 sensitive layers of the invention. Layers comprising mild reducing agents may also be added to promote thermal printer performance. Such layers may also

act to reduce emanation of any thermolysis products of laser imaging. Such layers can be applied by known means such as lamination or coating.

As indicated above, an image can be formed by the application of heat. Preferably, heat is applied locally, on irradiation with a laser. Suitable lasers
5 include those emitting at high energy, including Nd-YAG lasers and CO₂ lasers, the latter typically at a wavelength of 10,600 nm. In many cases, it may be desirable to use a low-energy laser, such as a diode laser, typically emitting light at a wavelength in the range of 800-1500 nm. In certain circumstances, this energy input may be insufficient to cause the desired reaction, and the
10 composition to be irradiated then preferably comprises a suitable absorbent material.

IR-absorbent materials are known. In general terms, any suitable such material may be incorporated, for the purposes of this invention, and can be chosen by one of ordinary skill in the art. A particularly preferred IR absorber for
15 use in the invention or any related technology is a conducting polymer, by which is meant a material that, in the polymerised state, comprises linked monomers (typically rings) that are conjugated and which can therefore allow delocalisation/conduction of positive or negative charge. The conjugation allows an absorption shift that can be controlled such that it applies to the wavelength
20 of irradiation, and which may also depend on the concentration of the polymer.

Examples of monomers that can be conjugated to give suitable conducting polymers are aniline, thiophene, pyrrole, furan and substituted derivatives thereof. Such polymers, in addition to providing the desired means of transferring heat from a low-power laser, have the advantage that they do not
25 readily diffuse out of the coating material. They can also act as the polymer binder. Yet another advantage of such materials is that they can be colourless, even at high loading (up to 5% by weight); this is by contrast to monomeric species that have been used, such as phthalocyanine, which absorb at about 800 nm but give the composition a greenish tinge, even at a loading of 0.1% by
30 weight.

Depending on the components to be irradiated, a black or coloured image may be obtained. The colour may be dependent on the irradiation power; thus, for example, a blue colour may be overpowered to black.

Multi-colour printing may also be achieved, e.g. using different colour-formers (and, if necessary, absorbers) responsive to different irradiation wavelengths. For example, UV, diode and CO₂ lasers may be used to give three-colour printing, by providing appropriate, different colour formers at different/overlapping locations on the substrate.

The initial colour of coating and image achieved on activation is not limited. Theoretically, any initial or final colour (red, blue, green, etc) is achievable and the energy required to develop the image (e.g. 100-140°C/2-4 Watts) can be controlled within a range. Additionally, a step-change of the image colour produced can be controlled with activation (e.g. 150-200°C/3-5 Watts), and so more than one distinct colour is possible from the same coating.

In general, the pigment can be one or more of a range of water-compatible materials as an ammonium octamolybdate.

The binder can be one or more of a range of water-soluble or amine-stabilised emulsion polymers, for a water-borne dispersion ink, or a solvent-soluble polymer for a solvent-borne dispersion or solution ink. Acrylic polymers can be used in each case.

Pigments can be water-dispersible inorganic or organic additives such as calcium carbonate etc.

One or more of a range of additives can be utilised, including surfactants or lubricants such as zinc stearate etc.

The IR-sensitive coating can be applied by a range of methods such as flood coating, flexo/gravure etc.

The IR-sensitive coating can be applied to a range of substrates such as self-adhesive label etc.

A protective layer of a film-forming water-borne top-coat ink can be applied onto the IR-sensitive coating.

The IR-absorber can be one or more of a range of water-compatible organic or inorganic materials, for a water-borne dispersion ink, or a solvent-

compatible, organic or inorganic material for a solvent-borne dispersion or solution ink (in the latter case, the material is preferably solvent-soluble).

In order that the invention may be more readily understood, reference is made to the following Examples, which are intended to be illustrative of the invention, but are not intended to be limiting in scope.

Examples 1 to 7

Solvent, water-based and UV-cure inks were formulated with ammonium octamolybdate (AOM). Lacquers were made in the proportions shown, coated onto cartonboard and dried. They were then marked using a scanning CO₂ laser with a beam diameter of 0.3 mm and a scan speed of 1000 mms⁻¹. The amounts used, and results, are shown in Table 1.

Example 8

197 g polypropylene homopolymer was blended with 3 g of a 4:1 mixture of AOM:Iridin 805, by mixing well on an Optiblender 2000 (Moulinex). The blend was compounded and palletised on a FOS axon extruder 11502 at temperatures of 190°C, 200°C, 210°C, 220°C and 225°C in the five respective zones. The moulded polymer could be marked with a CO₂ laser.

Examples 9 and 10

The procedure of Example 8 was followed, but using HDPE and HIPS, respectively. The moulded polymers could be satisfactorily marked with Nd-YAG and CO₂ lasers, respectively.

Example 11

An opaque white ink was formulated as below:

	Phenolic resin	17%
25	Colour Former	6%
	Binder	7%
	TiO ₂	6%
	Mica	2%
	Water	balance

30 This was printed by flexography to produce a panel on manila corrugate. The resulting white panel was exposed to the beam from a scribing CO₂ laser to produce a one-dimension bar code. The bar code was good quality, with class

AVB verification, when the black colour former Pergascript black I- R or Pergascript black I-2R (Ciba Speciality Chemicals) was used.

Example 12

5 A semi-opaque ink was formulated as described in Example 1, but without the pigment, and was gravure-printed onto white cartonboard. A scribing CO₂ laser was then used to produce alphanumeric and two-dimensional codes in the printed ink. The machine-readable code was of high quality when Pergascript black I-R, Pergascript Black I-2R or Pergascript Blue I-2G was used.

Example 13

10 An opaque ink was formulated as in Example 11 and patches were printed by flexography onto flexible packaging film (polypropylene). Alphanumeric codes were then written into the patches using both a scribing and a dot-matrix CO₂ laser.

Example 14

15 As in Example 13, patches were printed onto polypropylene film. The printed side of the film was then laminated with another sheet of polymeric material so that the printed patch was encapsulated. A CO₂ laser was then used to produce an alphanumeric code within the patch by exposure through the film.

Example 15

20 A lacquer was formulated, comprising of:

Polyvinyl chloride	30%
Ammonium octamolybdate	15%
Ethyl alcohol	balance

This was coated down onto aluminium foil, using a Meyer bar, and dried.
25 The semi-opaque coating was then exposed to a CO₂ laser beam of 0.3mm diameter sweeping at 1000 mm/second at an output power of 3W, to produce a black image.

Example 16

30 An opaque ink was formulated as given in Example 11, using a blue Colour Former but also with the addition of a small amount (0.4% by weight) of red pigment. The ink was printed by flexography onto white cartonboard, and the

resulting pink panel was exposed to the CO₂ laser beam. The image produced was purple.

Example 17

5	Ammonium heptamolybdate (AHM)	220 g
	Nitrocellulose DLX 3-5	250 g
	Ethanol	800 g
	Ethyl acetate	200 g

To a stirring solution of ethanol/ethyl acetate, nitrocellulose DLX 3-5 was added gradually. After the addition was complete the mixture was allowed stir at room temperature until a clear solution was obtained. Then a very fine powder of ammonium heptamolybdate was added portion-wise and after the addition was complete the mixture was stirred until uniform dispersion was achieved. This was coated down onto carton board, using a doctor blade, and dried. The semi-opaque coating was then exposed to a CO₂ laser beam of 0.3 mm diameter at a scan speed of 1000mm/second at an output power of 3-4 W, to produce a black image.

Example 18

20	Texicryl 13-576	100 g
	Ammonium heptamolybdate (AHM)	20 g
	Ammonia (25%)	0.5 g

To a stirring aqueous emulsion of Texicryl 13-567 (Ciba Speciality Chemicals), a fine powder of ammonium heptamolybdate was added gradually. After addition was complete, the mixture was stirred at room temperature until dissolution of ammonium heptamolybdate was obtained. This was coated down onto carton board, using a doctor blade, and dried. The semi-opaque coating was then exposed to a CO₂ laser beam of 0.3 mm diameter at scan speed of 1000mm /second at an output power of 3-4 W, to produce a black image.

Example 19

30	Ammonium Dimolybdate (ADM)	220 g
	Nitrocellulose DLX 3-5	250 g
	IMS	800 g
	Ethyl acetate	200 g

To a stirring solution of IMS (industrial methylated spirit)/ethanol/ethyl acetate, nitrocellulose DLX 3-5 was added gradually. After the addition was complete, the mixture was allowed to stir at room temperature until a clear solution was obtained. Then a very fine powder of ammonium dimolybdate was added portion-wise and, after the addition was complete, the mixture was stirred until a uniform dispersion was achieved. This was coated down onto carton board, using a doctor blade, and dried. The semi-opaque coating was then exposed to a CO₂ laser beam of 0.3 mm diameter at scan speed of 1000mm/second at an output power of 3-4 W, to produce a black image.

10 **Example 20**

Example 18 was repeated, using ADM instead of AHM and 0.3 g ammonia. Again, a black image was obtained.

Example 21

Example 19 was repeated, using ammonium paratungstate (APW) instead of ADM. Again, a black image was obtained.

Example 22

Example 20 was repeated, using APW instead of ADM. Again, a black image was obtained.

Example 23

Example 19 was repeated, using ammonium metatungstate instead of ADM. Again, a black image was obtained.

Example 24

Example 20 was repeated, using ammonium paratungstate instead of ADM. Again, a black image was obtained.

25 **Example 25 Water-borne Dispersion Inks**

The effect of the presence of an IR absorber in an ink formulation of the invention was determined. Blue and red water-based acrylic-emulsion inks of PVOH-stabilised dispersion (comprising PBI2RN or PRI6B colour former) were assessed.

30 A "standard" formulation of the invention was used, comprising the following proportions of components (% w/w):

Binder	26.5
Active Pigment	26.9
Fluid	46.6

Various "active" formulations were used, each containing the IR absorber
 5 Baytron P (HC Starck), a conducting polymer. The proportions of IR absorber
 used were 1.0, 2.5 and 5.0% (w/w). In, for example, formulations comprising
 5.0% Baytron P, the composition was:

	Binder	25.2
	Active Pigment	25.6
10	Fluid	44.2
	IR Absorber	5.0

The components were selected from:

	Binder	Gohsenol GH-17 polyvinyl alcohol and Texicryl acrylic emulsion;
15	Active Pigment	HC Starck AOM;
	Colour Former	Pergascript blue I-2RN crystal violet lactone and red I-6B;
	Fluid	water, dilute ammonium hydroxide etc; and
	IR Absorber	Baytron P

20 A 940 nm RoFin Dilas DF060 Diode Laser and K-bar 2.5-coated
 substrates were used for image forming.

The results are shown in Table 2. A good image was obtained when
 Baytron P was present.

Table 2

25	IR Absorber	Level (% w/w)	Unimaged	Imaged (940 nm)
	-	n/a	White	No Image
	-	n/a	"	"
	Baytron P	5.0	Off-white (slight)	Black Image
30	"	5.0	"	"

Samples of the blue ink formulations were coated with K-bar 2.5 onto Rafaltac Raflacoat (RC) and Hi-Fi polyester (PE) substrates. The coated substrates were then used for Nd:YAG (1064 nm) laser text imaging. Two formulations comprised Baytron P, two did not. The results are shown in Table 3.

Table 3

IR Absorber at 5.0% (w/w)	Substrate	Unimaged	Imaged (1064 nm)
-	RC	White	No Image
Baytron P	RC	Off-White (grey)	Black Text
-	PE	White	No Image
Baytron P	PE	Off-White (grey)	BlackText

The coatings in which Baytron P was absent gave no image or very faint text. PE-based samples gave better results than RC-based ones. Where images were obtained (i.e. when Baytron P was present), they were sharp and well-defined.

Example 26 Solvent-borne Dispersion Inks

Experiments similar to those of Example 25 were performed except that solvent-based inks were used.

The "standard" formulation was composed of (% w/w):

Binder	18.6
Active Pigment	22.3
Fluid	59.1

The "active" formulations contained the IR absorber Iriodin LS820 (Merck). The composition of the 5% (w/w) "active" formulation was:

Binder	16.7
Active Pigment	20.1
Fluid	53.2
IR Absorber	10.0

The results are shown in Table 4. Again, the presence of an IR absorber allowed image formation to occur.

Table 4

	Additive Type	Level % w/w	Unimaged	Imaged (940 nm)
5	-	n/a	White	No Image
	-	n/a	"	"
	-	n/a	"	"
	Iridin LS820	10.0	Off-white (slight)	"
	"	10.0	"	"
10	"	10.0	"	"
	"	10.0	Off-white (grey/green)	Black Image
	"	10.0	"	"
	"	10.0	"	"
	"	10.0	"	"

TABLE 1

EXAMPLE	BINDER	QUANTITY (g)	ADDITIVE	QUANTITY (g)	SOLVENT	QUANTITY (g)	LASER MARKING	
							POWER (W)	COLOUR OF IMAGE
1	Polyvinyl alcohol (Gohsenol GH17)	1.1	AOM	1	Water	9	3	Black
2	Alcotex 395B (26%)	12	AOM	2	Methanol/ methylacetate	-	3	Black
3	Ethyl Cellulose	2	AOM	2	Ethanol	15	3	Black
4	Klucel (hydroxy propyl cellulose)	2	AOM	2	Water	15	3	Black
5	Mowital B30H	2	AOM	2	Ethanol	10	3	Black
6	PVC Vycar 577E	15	AOM	3	Water	9	3	Black
7	Ebecryl 657 Ebecryl 1608	3.5 3.5	AOM	3	Irgacure 651 (Photoinitiator)	0.7	3	Black

Gohsenol was obtained from CIBA Specialty Chemicals

Alcotex was obtained from Harlow Chemicals

Klucel was obtained from Hercules

Mowital was obtained from Hoechst

Vycar was obtained from B.F. Goodrich

Ebecryl was obtained from UCB Chemicals

CLAIMS

1. A laser-markable composition which comprises a binder and an oxyanion of a multivalent metal.
2. A composition according to claim 1, wherein the binder comprises a labile group.
3. A composition according to claim 1 or claim 2, wherein the binder is a polymer.
4. A composition according to any preceding claim, wherein the metal oxyanion is ammonium octamolybdate.
5. A composition according to any preceding claim, which additionally comprises a colour-former, e.g. a substantially colourless electron-donating dye precursor.
6. A composition according to any preceding claim, which additionally comprises an IR absorber that absorbs laser radiation.
7. A transparent, dyed or pigmented printing ink or coating lacquer comprising the components defined in any of claims 1 to 6.
8. A melt-extrudable composition comprising the components defined in any of claims 1 to 6.
9. A polymer film obtainable by solvent-casting and comprising the components defined in claim 4.
10. A UV-curable medium comprising the components defined in any of claims 1 to 6.
11. An adhesive formulation comprising the components defined in any of claims 1 to 6.
12. A method for providing an image on a substrate, which comprises applying to the substrate a composition according to any of claims 1 to 6, followed by irradiation.
13. A method according to claim 12, wherein the irradiation is by means of a laser.
14. A method according to claim 13, wherein the oxyanion is of a multivalent metal that undergoes a colour change due to a change in oxidation state, on irradiation.

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15. A method according to claim 13 or claim 14, wherein the laser light has a wavelength of 800-1500 nm.
16. A method according to any of claims 13 to 15, wherein the composition comprises an IR absorber that absorbs laser radiation.
- 5 17. Use of a conjugated polymer as an IR absorber in a laser-markable composition or coating.





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